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<b>(21) International Application Number:</b> PCT/EP99/07769 <b>(22) International Filing Date:</b> 11 October 1999 (11.10.99)  <b>(30) Priority Data:</b> 98203407.6 12 October 1998 (12.10.98) EP  <b>(71) Applicant (for all designated States except US):</b> AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN SWIETEN, Andreas, Petrus [NL/NL]; Reinaldstraat 6, NL-6883 HM Velp (NL). WAANDERS, Petrus, Paulus [NL/NL]; Bentinckstraat 13, NL-7471 SL Goor (NL). MALTHA, Annemarieke [NL/NL]; De Meren 1729, NL-6605 XS Wijchen (NL).  <b>(74) Agent:</b> ARNOLD & SIEDSMA; Sweelinckplein 1, NL-2517 GK 's Gravenhage (NL).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> REDOX POLYMERIZATION PROCESS  <b>(57) Abstract</b>  A process for emulsion polymerization comprising the steps of reacting together a polymerization initiator, a reductor, and a polymerizable species, with the proviso that the polymerization initiator is not a hydroperoxide, characterized in that the polymerization initiator and the reductor are reacted together to provide a free radical moiety of the initiator, whereupon this free radical moiety initiates polymerization of the polymerizable species, this step being carried out at an initial cold start temperature, whereafter the temperature is increased to follow a temperature profile to a final preselected polymerization temperature.		

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## REDOX POLYMERIZATION PROCESS

The present invention relates to a process for emulsion polymerization, to the polymers obtainable by such a process, and to their uses.

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The production of water based resins, for example by means of emulsion polymerization techniques, is carried out thermally with inorganic persulfates. A problem with thermal polymerization is the process time, which leads to a less than desirable reactor output.

10

An object of the present invention is to provide an alternative polymerization process which aims to improve the process time.

The first aspect of the present invention provides a process according to claim 1.

15

Since the polymerization process according to the present invention provides a free radical initiator moiety by means of a redox reaction instead of by thermal decomposition, the polymerization can be carried out with a so-called "cold start", which involves the process time being reduced and the reactor output per unit

20

time being increased.

A redox polymerization is known for tertiary butyl hydroperoxide "Trigonox A-W70". The inventors have shown, however, that a redox polymerization utilizing other organic peroxides provides unexpectedly good results.

25

The inventors have shown that polymerization can start at a lower initial temperature, which means that because of the longer "heating-up" time necessary in thermal polymerization, the polymerization time can be reduced utilizing the process of the current invention.

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The inventors have furthermore demonstrated that the process according to the present invention enables a polymer with a very low residual monomer level to be

obtained, whilst, with respect to thermal polymerization, the amount of initiator used can be reduced.

Good results have been achieved under the conditions as defined in claims 2-6.

5

The polymerization initiator is most preferably a substantially non-water-soluble initiator, such as defined in claim 7 or 8, since these non-water-soluble initiators yield an unexpectedly high efficiency in polymerization.

10 This higher efficiency results in shorter polymerization times and in polymer resins with improved properties. The higher efficiency of the organic peroxides is expressed by the low level of residual monomers and by the low molecular weights ( $M_w/M_n$ ) of the polymers formed.

15 Furthermore, the conductivity of the resins initiated with the organic peroxide/redox system is lower than for corresponding resins that were initiated by persulfates.

The reductor of the redox system preferably is chosen from the following group:  
20 sodium formaldehyde sulfoxylate (SFS), sodium bisulfite, Ascorbic acid (vitamin C), aldehydes, for example glutaraldehyde, sodium metabisulfite, sodium dithionate, and sugars, wherein the reductor most preferably is sodium formaldehyde sulfoxide.

25 The polymerizable species preferably is chosen from the following group: acrylonitrile, acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methoxyethyl acrylate, dimethyl aminoacrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, stearic  
30 methacrylate, dimethyl aminomethacrylate, allyl methacrylate, 2-hydroxyethyl

acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, acrylamide, methacrylamide, glycidyl acrylate, vinyl ester of versatic acid, styrene, para-methyl styrene, vinyl acetate, alpha-methyl styrene, wherein the polymerizable species most preferably comprises vinyl acetate  
5 and/or the vinyl ester of versatic acid.

Further preferred process conditions are detailed in claims 11-15.

The polymerization is carried out in a conventional emulsion, for example in a  
10 mixture of anionic and non-ionic surfactants such as Witconate (sodium alpha-olefin sulfonate) and Syntopon (ethoxylated nonylphenol); however, other emulsifiers or mixtures are also possible.

This emulsifier solution preferably is a mixture of nonionic and anionic emulsifiers  
15 and most preferably is selected from the group consisting essentially of:

- long-chain aliphatic carboxylates (ionic)
- alkylbenzene sulfonates (ionic)
- alkyl sulphates (ionic)
- dialkylsulphosuccinate (ionic)
- 20 - ethoxylated alcohols (nonionic)
- ethoxylated alkyl phenols (nonionic)
- ethoxylated amine or amides (nonionic).

A second aspect of the present invention provides a polymer obtainable  
25 according to this process.

The invention will now be further elucidated by way of the following examples. Examples 1-6 are comparative examples and Examples 7-12 are examples according to the present invention using a redox system. Examples 3, 4, 6, 8-12  
30 were subjected to a temperature profile increasing from an initial temperature to a

final temperature, i.e. subjected to a so-called "cold-start", and Example 7 was carried out at constant temperature.

#### Procedure of preparation

- 5 The polymerization in all the examples was carried out in a 0.25 L glass reactor with a stirrer under nitrogen. A seed was prepared first by adding 10% of the reactive components at polymerization temperature.

The preparation of the seed was carried out as follows:

- 10 The reactor was filled with buffered (NaAc/HAc) emulsifier solution (Witconate/Syntopon), prepared with oxygen-free deionized water. At the polymerization temperature 10% of the pre-emulsion containing soaps (Witconate and Syntopon), monomers, and, in the case of the redox system according to the present invention, also reductor and catalyst, were added. In addition the solution  
15 or pre-emulsion of the initiator was added to achieve control over the accurate dosing of the initiator.

- After a polymerization time of 30 minutes the remaining monomers, pre-emulsion, and initiator solution were dosed in 2.5 hours. In Examples 3, 4, 6, 8-12 the  
20 temperature was increased to the final temperature in the same period, following a temperature profile. The final temperature was maintained for 1 hour.

The composition of the buffered soap solution used was as follows:

	NaAC.3aq	0.25 g (sodium acetate)
25	HAc	0.11 g (acetic acid)
	H <sub>2</sub> O	30.3 g
	Witconate	0.38 g (soap)
	Syntopon	0.38 g (soap)

Example 1

## Thermal system

The temperature was kept at 70°C during the polymerization. The composition of the used pre-emulsion was:

Witconate	1.28 g
Syntopon	1.28 g
H <sub>2</sub> O	34.43 g
Vac (vinyl acetate)	52.5 g (monomer)
VEOVA (vinyl ester of versatic acid)	22.5 g (monomer)

5

The initiator solution was composed of 4.18 mmoles ammonium/sodium or potassium persulfate in 25 g H<sub>2</sub>O. The total process time including the time needed for heating up the reactor contents to 70°C before polymerization amounted to 5.5 hours.

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Examples 2, 5, 7

The temperature was kept at 70°C (Examples 2, 5) and 20°C (Example 7), respectively. The composition of the used pre-emulsions was as follows:

Witconate	1.28 g
Syntopon	1.28 g
H <sub>2</sub> O	34.43 g
Peroxide	1.04-4.18 mmoles as mentioned in the examples
Vac (vinyl acetate)	52.5 g (monomer)
VEOVA (vinyl ester of versatic acid)	22.5 g (monomer)

- 15 The reductor SFS (sodium formaldehyde sulfoxyde: 0.65 g) and the catalyst (FeSO<sub>4</sub> 16.7 mg) were dissolved in 25 g H<sub>2</sub>O.  
The total process time was 4 hours.

Examples 3, 4, 6, 8-12

The polymerization temperature was kept at 20°C for the first 30 minutes to prepare a seed. The temperature was then increased by 20°C/hour to 70°C following a temperature profile.

5

It is noted that other starting temperatures and temperature programmes can be used, either for initiating polymerization or for initiating and completing polymerization.

10 In all the examples the residual monomers were determined by gas chromatography (GC). The molecular weight of the prepared polymers was determined by gel permeation chromatography (GPC) with polystyrene for calibration. The conversion/solids content was determined by standard procedure. The viscosity was determined using a Brookfield digital viscometer.

15

The results are shown in Table 1.

Examples 13-2420 Procedure of preparation

The polymerization in all examples was carried out in a 0.25 L glass reactor with a stirrer under nitrogen. A seed was prepared first by adding 10% of the reactive components at polymerization temperature.

25 The preparation of the seed was carried out as follows:

The reactor was filled with the emulsifier solution (sodium lauryl sulfate in water) prepared with oxygen-free deionized water. At the starting polymerization temperature 10% of the pre-emulsion containing soap, monomers, and in the case of the redox system, also reductor and catalyst, were added. In addition the  
30 solution or pre-emulsion of the initiator was added to achieve control over the



accurate dosing of the initiator.

After a polymerization time of 30 minutes the remaining monomers, pre-emulsion, and initiator solution were dosed in 2.5 hours. The temperature was increased to  
5 the final temperature in the same period, following a temperature profile. The final temperature was maintained for 1 hour.

The composition of the soap solution was as follows:

0.10 g sodium lauryl sulfate (emulsifier)  
10 25.0 ml deionized water

Pre-emulsion:

1.60 g sodium lauryl sulfate  
30 ml deionized water  
15 70 g monomer mixture (butylacrylate / styrene / methacrylic acid = 6/4/0.1)  
including the initiator (1.04 meq), if not water-soluble.

The reductor SFS (sodium formaldehyde sulfoxylate 0.16 g) and the catalyst ( $\text{Fe}^{II}\text{SO}_4$  2.8 mg) were dissolved in 10 ml water.

20 The molar ratio oxidator: reductor: Fe = 1: 1: 0.01

The results are shown in Tables 2 and 3.

Table 1

Example	Initiator	meq oxid.	conditions	residual Vac%	residual VeoVa %	Mw/Mn x1000	$\eta$ mS/cm	PS (nm)
1	K2S2O8	4.2	70°C thermal	0.10	0.074	630/50	5.3	180
2	K2S2O8	4.2	70°C redox	0.51	0.23	410/37	9.8	212
3	K2S2O8	4.2	20 → 70°C redox	0.27	0.095	790/64	10.3	197
4	K2S2O8	2.1	20° → 70°C redox	0.36	0.12	740/49	5.6	128
5	Tx A-W70 (tert-Butyl hydroperoxide)	4.2	70°C redox	0.096	0.30	290/19	3.4	189
6	Tx A-W70 (tert-Butyl hydroperoxide)	4.2	20 → 70°C redox	0.073	0.028	670/44	3.6	141
7	Tx 21 (tert-Butyl peroxy-2- ethylhexanoate)	4.2	20°C redox	0.054	0.067	170/18	3.1	143
8	Tx C (tert-Butyl peroxybenzoate)	4.2	20 → 70°C redox	0.17	0.11	150/22	3.2	175
9	Tx C (tert-Butyl peroxybenzoate)	2.1	20° → 70°C redox	0.049	0.03	270/35	2.2	190
10	Tx C (tert-Butyl peroxybenzoate)	1.5	20° → 70°C redox	0.082	0.022	560/48	1.9	181
11	Tx C (tert-Butyl peroxybenzoate)	1.05	20° → 70°C redox	0.048	<0.004	1000/48	1.7	148
12	Tx C (tert-Butyl peroxybenzoate) Without Fe2+	4.2	20 → 70°C redox	<0.016	0.009	770/106	3.1	172

Table 2 Emulsion:  
Theoretical solids content: VeoVa10/VAc-emulsions: 44%  
Reductant: SFS/Fe(II) Ox : SFS : Fe = 1 : 1 : 0.01

Initiator	Monomers	[Initiator] meq	Solids	Residual monomers VeoVa	Vac	Mw	Mn	D	pH
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	VeoVa/VAc	1.4	39.8	0.65	1.23	482900	51900	9.30	2.30
	VeoVa/VAc	2.1	43.2	0.34	0.13	412000	59000	6.9	2.30
Tx C	VeoVa/VAc	1.4	42.2	n.d.	0.64	211300	33300	6.34	4.35
Tx 22	VeoVa/VAc	2.8	40.5	0.97	0.26	695000	99600	6.98	3.61
Tx 117	VeoVa/VAc	1.4	42.5	n.d.	n.d.	278200	31400	8.85	4.55
Laurox	VeoVa/VAc	1.4	16.5	n.d.	n.d.	728500	141500	5.15	4.10

n.a. = not applicable

n.d. = not detected

Table 3 Emulsion:  
Theoretical solids content: STY/BA/MA-emulsions:46%  
Reductant: SFS/Fe(II) Ox : SFS : Fe = 1 : 1 : 0.01

Initiator	Monomers	[Initiator] meq	Solids	Residual monomers STY BA	Mw	Mn	D	pH
$K_2S_2O_8$	STY/BA/MA	1.04	44.8	n.d.	1753000	346000	5.07	2.19
Tx C	STY/BA/MA	2.08	45.1	n.d.	690000	169000	4.1	2.0
	STY/BA/MA	1.04	48.3	0.04	713700	144300	4.95	4.20
Tx 22	STY/BA/MA	2.08	50.0	n.d.	529500	70900	7.47	1.92
Tx 117	STY/BA/MA	1.04	47.0	0.10	536080	140400	3.82	4.40
Laurox	STY/BA/MA	1.04	45.5	n.d.	2367400	426300	5.55	6.30

n.a. = not applicable

n.d. = not detected

Styrene/butyl acrylate/methacrylic acid : 4/6/0.1

Tx C = tert-butyl peroxybenzoate

Tx 22 = 1,1 di(tert-butylperoxy)cyclohexane

Tx 117 = tert-butylperoxy-2-ethylhexyl carbonate

Laurox = di-lauroyl peroxide

### Results

As reference the emulsion copolymerization of vinylacetate and VeoVa with potassium persulfate at 70°C was used (thermal conditions).

5

The results show low residual monomer levels for the non-water-soluble organic peroxides (peroxyesters) under redox conditions. As the efficiency of the non-water-soluble peroxyesters such as Trigonox C was much higher than that of the water-soluble persulfates and hydroperoxides, the levels of addition  
10 could be lowered to 20-40% of the original milli-equivalents of initiator used. Due to lower amounts of initiator and reductor, a higher value for pH and lower values for the conductivity were obtained. The prepared polymer had molecular weights (Mw/Mn) comparable with those of the reference copolymer of VeoVa/VAc.

15

The peroxyesters such as Trigonox 21 gave a high conversion of monomers at ambient temperature.

The invention is not limited to the above description; rather, the requested  
20 rights are determined by the following claims.

**CLAIMS**

1. A process for emulsion polymerization comprising the steps of reacting together a polymerization initiator, a reductor, and a polymerizable species, with the proviso that the polymerization initiator is not a hydroperoxide, characterized in that the polymerization initiator and the reductor are reacted together to provide a free radical moiety of the initiator, whereupon this free radical moiety initiates polymerization of the polymerizable species, this step being carried out at an initial cold start temperature, whereafter the temperature is increased to follow a temperature profile to a final preselected polymerization temperature.
2. Process according to claim 1 carried out at an initial temperature of up to 70°C, for example carried out at an initial temperature of up to 50°C and preferably of up to 35°C.
3. Process according to claim 1 or 2 carried out at an initial temperature lying in the range of +10° to 35°C, preferably in the range of 15° to 25°C.
4. Process according to any one of the preceding claims wherein the initial temperature is maintained for a predetermined length of time, for example up to 2 hours, preferably up to 1 hour, most preferably up to half an hour.
5. Process according to any one of the preceding claims wherein the temperature is increased subsequent to the initial temperature maintenance period to follow a temperature profile to a final polymerization temperature, preferably up to a final polymerization temperature of at the most 90°C, and wherein the final polymerization temperature preferably lies in the range of 50-80°C and most preferably is

70°C or less.

- 5 6. Process according to claim 5 wherein the initial temperature is increased incrementally per pre-selected time period, preferably by about 20°C per hour.
- 10 7. Process according to claim 6 wherein the initiator is selected from the group consisting essentially of: diisobutanoyl peroxide, cumyl peroxyneodecanoate, 2,4,4-trimethylpentyl-2-peroxyneodecanoate, tert-amyl peroxyneodecanoate, bis(4-tert-butylcyclohexyl)peroxydicarbonate, bis(-ethylhexyl)peroxydicarbonate, tert-butyl peroxyneodecanoate, dibutyl peroxydicarbonate, dicetyl peroxydicarbonate, dimyristyl peroxydicarbonate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, bis(3,5,5-trimethylhexanoyl) peroxide, dilauroyl peroxide, didecanoyl peroxide, 2,5"-
- 15 bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-amyl peroxy-2-ethylhexanoate, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, 1,4-bis(tert-butylperoxycarbo)cyclohexane, tert-butyl peroxyisobutanoate, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, tert-butyl
- 20 peroxy-3,5-trimethylhexanoate, 2,2-bis(tert-butylperoxy)butane, tert-butylperoxy isopropyl carbonate, tert-butylperoxy 2-ethylhexyl carbonate, tert-butyl peroxyacetate, tert-butyl peroxybenzoate, di-tert-amyl peroxide, dicumyl peroxide, bis(tert-butylperoxyisopropyl)benzene, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, tert-butyl cumyl peroxide, 2,5-bis(tert-
- 25 butylperoxy)-2,5-dimethyl-3-hexyne, and di-tert-butyl peroxide.
8. Process according to claim 7 wherein the initiator is substantially non-water-soluble and is selected from the group consisting essentially of:
- alifatic and aromatic peroxyesters, preferably tert-butyl peroxy-2-

ethylhexanoate (Trigonox 21), tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxybenzoate (Trigonox C), tert-amyl peroxybenzoate, tert-butyl peroxyacetate, tert-butyl peroxy-3,5-trimethylhexanoate, tert-butyl peroxyisobutanoate, tert-butyl peroxydiethylacetate, tert-butyl peroxy-pivalate;

- peroxycarbonates, preferably tert-butyl peroxyisopropyl carbonate (Trigonox BPIC), and tert-butyl peroxy-2-ethyl hexyl carbonate Trigonox 117).

9. Process according to any one of the preceding claims wherein the reductor is chosen from the group consisting essentially of: sodium formaldehyde sulfoxylate (SFS), sodium bisulfite, Ascorbic acid (vitamin C), aldehydes, for example glutaraldehyde, sodium metabisulfite, sodium dithionate, and sugars.

10. Process according to any one of the preceding claims wherein the polymerizable species is selected from the group consisting essentially of: acrylonitrile, acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methoxyethyl acrylate, dimethyl aminoacrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, stearic methacrylate, dimethyl aminomethacrylate, allyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, acrylamide, methacrylamide, glycidyl acrylate, vinyl ester of versatic acid, styrene, para-methyl styrene, vinyl acetate, alpha-methyl styrene.

11. Process according to any one of the preceding claims carried out in the presence of a catalyst, said catalyst preferably being a water-soluble salt



derived from a transition metal, and most preferably being selected from the group consisting essentially of  $\text{Fe}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cu}^+$ , and  $\text{Ce}^{3+}$ .

- 5 12. Process according to any one of the preceding claims wherein the initiator and the reductor are provided in the following ratios 10:1 to 1:5, preferably 4:1 to 1:2.
13. Process according to any one of the preceding claims wherein the ratio of catalyst: oxidator is about 0-0.1 on a molar basis.
- 10 14. A polymer obtainable according to the process of any one of the preceding claims.
- 15 15. Polymer according to claim 14 having one or more of the following characteristics:
- a conductivity lower than about 5,
  - a low residual monomer level,
  - a particle size of less than about 220 nm, preferably less than 200 nm.
- 20 16. Use of a polymer according to claims 14 and/or 15 in coatings and/or adhesives.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/07769

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F4/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 022 281 A (E. S. SMITH) 20 February 1962 (1962-02-20) claim 1	1
A	GB 1 558 835 A (JAPAN SYNTHETIC RUBBER CO.) 9 January 1980 (1980-01-09)	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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